



# Light-induced X,W-band Electron Spin Resonance study of double-crystalline donor-acceptor P3HT-b-PPerAcr block copolymers in solid thin films



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## ABSTRACT

Light-induced X,W-band Electron Spin Resonance (LESR) study of double-crystalline donor-acceptor block copolymers (BCPs) comprised of poly-3-hexylthiophene as the donor and poly-perylene bisimide acrylate as the acceptor segments is presented. It is suggested that, while the intrinsic light-induced charge separation efficiency in the BCPs registered by LESR could be more efficient than in bulk heterojunction solar cells based on the P3HT/PCBM blends, the photovoltaic performance of the BCPs is limited significantly by the incorrect orientation of crystalline  $\pi$ -stack morphology of (poly-perylene bisimide acrylate) domains.

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## 1. Introduction

Organic solar cells have been a topic of intensely pursued interdisciplinary research during the last decade. The successful application of solution-processed blends of soluble  $\pi$ -conjugated polymers and fullerene derivatives as the active layer along with continued device optimization has led to remarkable progress, leading to an increase in conversion efficiency to 10% since the realization of first bulk heterojunction solar cell [1–4]. In spite of the recent advancements, the performance of bulk heterojunction (BHJ) solar cells still critically depends on the physical interaction of the donor and acceptor components, i.e., on the blend morphology of the composite [5–7]. There is a common understanding that ideal morphology of polymer solar cells requires interpenetrating networks of donor and acceptor materials forming domains of dimensions compatible with the exciton diffusion length and that are coarse enough to provide efficient charge transporting channels [8,9]. Extensive work on blended solar cells has shown that the possibility to achieve this morphology from any material combination requires serious optimization of a multitude of processing parameters [5,10,11].

In addition to the tedious task of realizing an optimized morphology, polymer-fullerene blends are known for continuous uncontrolled phase segregation of donor and acceptor components and an unstable morphology at elevated temperatures [12,13].

To overcome these problems, many new approaches have evolved to fix the nanoscale morphology of components [13–15]. The direct approach is, however, to use block copolymers (BCPs) where dissimilar polymer blocks with donor and acceptor functionalities are joined together by covalent bonds and thus preventing large scale phase separation. The BCPs are also known to segregate into disparate blocks of the polymer constituents and form nanometer length scale patterns through a minimization of free energy, a process known as microphase separation [16]. Thus, the application of BCPs offers a possibility for the design of highly ordered self-assembled nanoscale phase separated structures, addressing the morphology issues of polymer blends.

In initial works, several approaches have been pursued by incorporating both donor and acceptor functionalities into the different blocks of a BCP. Heiser et al. and de Boer et al. demonstrated bi-functional BCP for photovoltaic applications in which a donor PPV block is attached to a polystyrene block with pendant C<sub>60</sub> [17,18]. Later on, Lindner et al. demonstrated several classes of donor-acceptor block copolymers by means of nitroxide-mediated radical polymerization [19–21]. In these block copolymers perylene-diimide acceptor groups attached to polyacrylate

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